PB87-191821

Determination of Emission Rates and Concentration Levels of p-Dichlorobenzene from Moth Repellant

Acurex Corp., Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

May 87

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA/600/D-87/165
May 1987

PB87-191821

DETERMINATION OF EMISSION RATES AND CONCENTRATION LEVELS OF p-DICHLOROBENZENE FROM MOTH REPELLANT

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EPA Contract 68-02-3988

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U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-87/165		PB87-191821/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
Determination of Emission Rates and Concentration Levels of p-Dichlorobenzene from Moth Repellant	May 1987
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Leonard H. Nelms and Mark A. Mason (Acurex) and Bruce A. Tichenor (EPA/AEERL)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Acurex Corporation P.O. Box 13109 Research Triangle Park, North Carolina 27709	11. CONTRACT/GRANT NO. 68-02-3988, Task 80
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711	Published Paper; 5-11/86 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is Bruce A. Tichenor, Mail Drop 54, 919/541-2991.

16. ABSTRACT The paper describes a recently completed EPA study of the emissions of p-dichlorobenzene from moth repellant. This product, commonly used by the general population to protect garments from insect damage, is widely available. Samples, in cake form, were purchased from a local department store for testing under conditions simulating the manufacturer's recommended usage. Temperature, relative humidity, and air exchange rates for each test were selected to investigate their effects on the rate of emission of p-dichlorobenzene from the product. Data were gathered using each set of test conditions for a period of time sufficient for the concentration in the chamber to stabilize. Emission rates were calculated and used to investigate the effects of the environmental variables.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Measurement	Pollution Control	13B
Emission	Stationary Sources	14G
Mothproofing	p-Dichlorobenzene	13H
Chlorobenzenes	Organic Vapors	07C
Organic Compounds	Consumer Products	
Test Chambers		14B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	15
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

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INTRODUCTION

The US EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, is conducting studies on the emissions of organic vapors from building materials and consumer products. [1,2,3] This test program involves the use of small environmental test chambers with control of temperature, relative humidity, and air exchange rate. The chambers are constructed of electropolished stainless steel; complete mixing is provided by a fan.[4]

Recently, a study of the emissions of p-dichlorobenzene from moth repellant was completed. This product is commonly used by the general population to protect garments from insect damage and is widely available. Samples, in cake form, were purchased from a local department store for testing under conditions simulating the manufacturer's recommended usage. Temperature, relative humidity, and air exchange rates for each test were selected to investigate their effects on the rate of emission of p-dichlorobenzene from the product. Data were gathered using each set of test conditions for a period of time sufficient for the concentration in the chamber to stabilize. Emission rates were calculated and used to investigate the effects of the environmental variables.

EXPERIMENTAL METHODS

Environmental parameters for the planned experiments were chosen to reflect typical residential conditions. Temperature and relative humidity were varied over normal seasonal ranges. The air exchange rates were varied over a range [0.25 to 2.0 air changes per hour (ACH)] to represent expected conditions. Table I is the test matrix. Chamber loading was set to match that recommended by the manufacturer. The instructions provided with the product suggest using one cake per 0.34 m^3 (12 ft^3) of space treated. Since the test chamber volumes are 0.166 m^3 (5.9 ft^3), half a cake was used for each test. Each sample had an estimated surface area of 55 cm^2.

Chamber Testing

Prior to each test, the chambers and other system components were cleaned by thoroughly washing them with methanol, followed by rinsing with deionized water, then high purity water. The chambers were then dried and installed in the incubator where temperature was controlled. Following at least 24 hours, chamber blanks were collected and analyzed, to ensure that the chambers were clean.

The moth crystal cakes were cut in half, weighed, and placed in the chamber. Frequent sampling of the chamber exhaust during the initial stages of the test was required to observe the rapidly changing concentrations, followed by a reduction in frequency as the concentration leveled

off. Once the analyst felt that the concentration was stabilized, sampling was discontinued. After chamber cleaning, another experiment was started using a different set of environmental conditions and a new sample of the material.

Sample Analysis

The moth repellant was a relatively pure chemical compound, 1,4-dichlorobenzene. An internal standard, hexane, was added to the sample stream through a port in a 1 liter glass mixing flask just downstream of the test chamber. Samples were taken from a glass manifold connected to the mixing flask. Sampling occurred by drawing a portion of the air stream through a heated valve (175°C) equipped with dual calibrated sampling loops or by drawing a sample from the manifold with a 5 cc gastight syringe. In each case, the sample was injected into a 2.4 m (8 ft) long by 2 mm (0.1 in.) ID stainless steel gas chromatograph (GC) column packed with 1% SP-1000 on Carbopack B (60/80 mesh). Data were collected on a microprocessor-based data station running software developed specifically for GC. The output signal from the flame ionization detector (FID) was digitized and stored for further processing.

Environmental Data

All chamber parameters (temperature, relative humidity, air flow rate) were monitored using a second microprocessor-based system. This system also provided feedback control of some of the parameters. These data were stored by the computer system for subsequent analysis.

RESULTS

Following the completion of a GC analysis, the stored data were processed by the GC data station. The GC data was reduced to generate the area of each peak of interest, so it could be quantified. These peak areas were used, with internal standard calculation procedures, to determine the amount of p-dichlorobenzene contained in each sample according to:

$$C_x = (A_x) \times (R_x) \times (C_{ia}/C_{im}) \qquad (1)$$

where:

C_x = concentration of p-dichlorobenzene (ug/m^3)
A_x = peak area for p-dichlorobenzene (counts)
R_x = response factor for p-dichlorobenzene (ug/m^3-count)
C_{ia} = actual concentration of internal standard (ug/m^3)
C_{im} = measured concentration of internal standard (ug/m^3)

For each experiment, the concentration in the chamber exhaust was calculated and the results plotted versus time. Figure 1 is a typical plot. Table II summarizes the data for 14 test runs. The right-hand column of Table II is the concentration determined by averaging the data on the plateau portion of the plots of concentration versus time.

Emission Factors

The emission rate for the moth crystal cake can be calculated by:

$$E = (C) \times (F/A) \qquad (1)$$

where:

E = emission rate for p-dichlorobenzene (ug/cm^2-hr)
C = concentration of p-dichlorobenzene (ug/cm^3)
F = flow rate through chamber (m^3/hr)
A = area of the sample (cm^2)

Dunn and Tichenor[5] present a model that accounts for chamber concentration (i.e., evaporation suppression due to reduced vapor pressure driving force) and "wall effects." Table III compares the emission rates calculated with both techniques. The right-hand column shows the percent difference between the two estimates. In all but two tests, the estimates agree within 10%.

There is substantial evidence that the interior surfaces of the chamber acted as a sink for the p-dichlorobenzene. After completion of tests MC10.1 and MC11, efforts were made to determine the amount of 1,4-dichlorobenzene that remained on the chamber walls. These efforts involved carefully washing the chamber walls with methanol (i.e., the first step in the chamber cleaning process) and recovering the solvent. The volume of solvent was measured, and an aliquot injected onto the GC column for analysis. The results confirmed that material was adsorbed on the walls. For test MC10.1, about 160 mg of 1,4-dichlorobenzene was recovered from the walls, while about 23 mg was recovered for MC11. The final average concentrations for these two tests were 5,300 and 1,170 mg/m^3, respectively. Thus, there was a substantial amount of material adsorbed on the chamber walls during the experiments, and this amount appeared to be related to the vapor phase concentration. Since the model[5] accounts for this phenomenon, it is felt that the emission rates estimated from the model should be used.

Effect of Temperature

The moth crystal cakes were essentially pure p-dichlorobenzene, which sublimes from the solid state at room temperature. The effect of temperature on the emission rate depends to a great extent on the relationship between vapor pressure and temperature. Figure 2 shows the estimated equilibrium concentration of p-dichlorobenzene as a function of temperature based on

vapor pressure data from Perry.[6] For the two temperatures evaluated, 23 and 35°C, the equilibrium concentrations are 4,300 and 13,600 mg/m^3, respectively. Thus, temperature has a strong effect on the evaporation potential from the cake. This is confirmed by the experimental data. Figure 3 shows the emission rate versus air exchange for both 23 and 35°C. Obviously, temperature has a dramatic effect on emission rates.

Effect of Air Exchange Rate

Figure 3 also shows that the emission rate increases as the air exchange rate increases. This is basically caused by the increase in vapor pressure driving force due to the lower chamber concentrations at the higher air exchange rates.

Effect of Relative Humidity

Preliminary evaluation of the data indicated no effect of relative humidity on emission rate. However, subsequent evaluation using regression analysis showed that an increase in relative humidity is accompanied by a decrease in emission rate. Dunn and Tichenor[5] provide further details. This effect of relative humidity is consistent with that predicted for formaldehyde emissions from particleboard using the Berge equation.[7]

Quality Assurance

The analyses were run using an internal standard for the quantification of p-dichlorobenzene. This internal standard was also used to evaluate the success of the analytical program. The relative standard deviation of the absolute concentration values of the internal standard was used as an indication of operator/method precision. The average recoveries of the internal standards within each experiment ranged from 87 to 113%. The overall average recovery for this series of experiments was calculated to be 101%. The overall standard deviation was found to be 12.4%, and the relative standard deviation was 12.3%. These values are within the limits set forth by the Quality Assurance Project Plan (QAPP) which was adopted for these experiments.

Three sets of replicate analyses were conducted, and the emission rates are shown in Figure 4. The emission rates used in Figure 4 are those calculated using the model, except for test MC8 for which a model estimate is not available. As shown in this plot, the reproducibility of the data is reasonable.

CONCLUSIONS

Emission rates of p-dichlorobenzene from moth crystal cakes were determined based on testing in small (166 liter) test chambers. The positive effects of temperature and air exchange rate on the emission rates are clearly shown by examining the data. The negative effect of relative humidity is more subtle and required regression analysis for its determination. Quality assurance procedures, including replicate samples, indicate data with reasonable accuracy and precision.

ACKNOWLEDGMENTS

This work was done under EPA contract 68-02-3988 to Acurex Corporation. The authors wish to thank S. N. Bailey, C. M. Plunkett, and M. C. Newhall of Acurex for their assistance in sample collection, analysis, and data processing.

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Table I. Test matrix for moth crystal experiments.

Test No.	Temperature (°C)	Relative Humidity (%)	Air Exchange Rate (hr^{-1})	Season
MC7	23	20	0.25	Winter
MC4	23	20	0.50	Winter
MC3	23	20	1.0	Winter
MC6	23	50	0.25	Spring
MC8	23	50	1.0	Spring
MC14	23	50	2.0	Summer
MC9	35	20	0.25	Summer
MC10	35	50	0.25	Summer
MC11	35	20	1.0	Summer
MC12	35	50	2.0	Summer
MC13	35	50	0.50	Summer
MC5	23	20	0.50	Replicate of MC4

Table II. Summary of moth crystal experimental data.

Test No.	Test Duration (min.)	Average Temp. (°C)	Average RH (%)	Average Flow (l/min.)	Air Exchange (hr^{-1})	Average Conc.[a] (ug/m^3)
MC3	4210	23.4	15.2	2.70	0.98	540,000
MC4	1110	23.2	14.9	1.37	0.50	868,000
MC5.1[b]	1079	23.3	17.5	1.39	0.50	1,040,000
MC6.1[b]	1079	22.9	51.7	0.71	0.26	1,500,000
MC7	5475	23.3	19.3	0.79	0.29	1,190,000
MC8	4153	22.8	54.0	2.77	1.00	488,000
MC8.1[c]	1550	22.6	53.1	2.75	0.99	538,000
MC9	1326	35.5	14.8	0.76	0.27	5,060,000
MC10	1326	35.6	34.0	0.69	0.25	5,200,000
MC10.1[c]	1407	35.6	50.3	0.70	0.25	5,300,000
MC11	1407	35.4	18.1	2.74	0.99	1,710,000
MC12	1494	36.3	49.7	5.32	1.92	986,000
MC13	1313	35.4	54.8	1.36	0.49	2,880,000
MC14	4349	24.8	42.5	5.30	1.92	313,000

[a] Based on "plateau" of concentration vs. time curve.

[b] MC5.1 and MC6.1 replace tests MC5 and MC6 which were curtailed due to experimental problems.

[c] Replicate tests.

Table III. Emission rates of p-dichlorobenzene from moth crystal cakes (ug/cm^2-hr).

Test No.	Based on Average Conc.	Based on Model[5]	Difference (%)[a]
MC3	1590	1630	2.5
MC4	1300	1490	12.8
MC5.1	1580	1600	1.3
MC6.1	1160	1260	7.9
MC7	1030	1080	4.6
MC8	1470	NA[b]	-
MC8.1	1620	1620	0.0
MC9	4200	4250	1.2
MC10	3920	4100	4.4
MC10.1	4050	4700	13.8
MC11	4870	5200	6.3
MC12	5740	6080	5.6
MC13	4290	4390	2.3
MC14	1810	1780	-1.7

[a] [(Col. 3 - Col. 2)/Col. 3] x 100%

[b] NA = Not Available

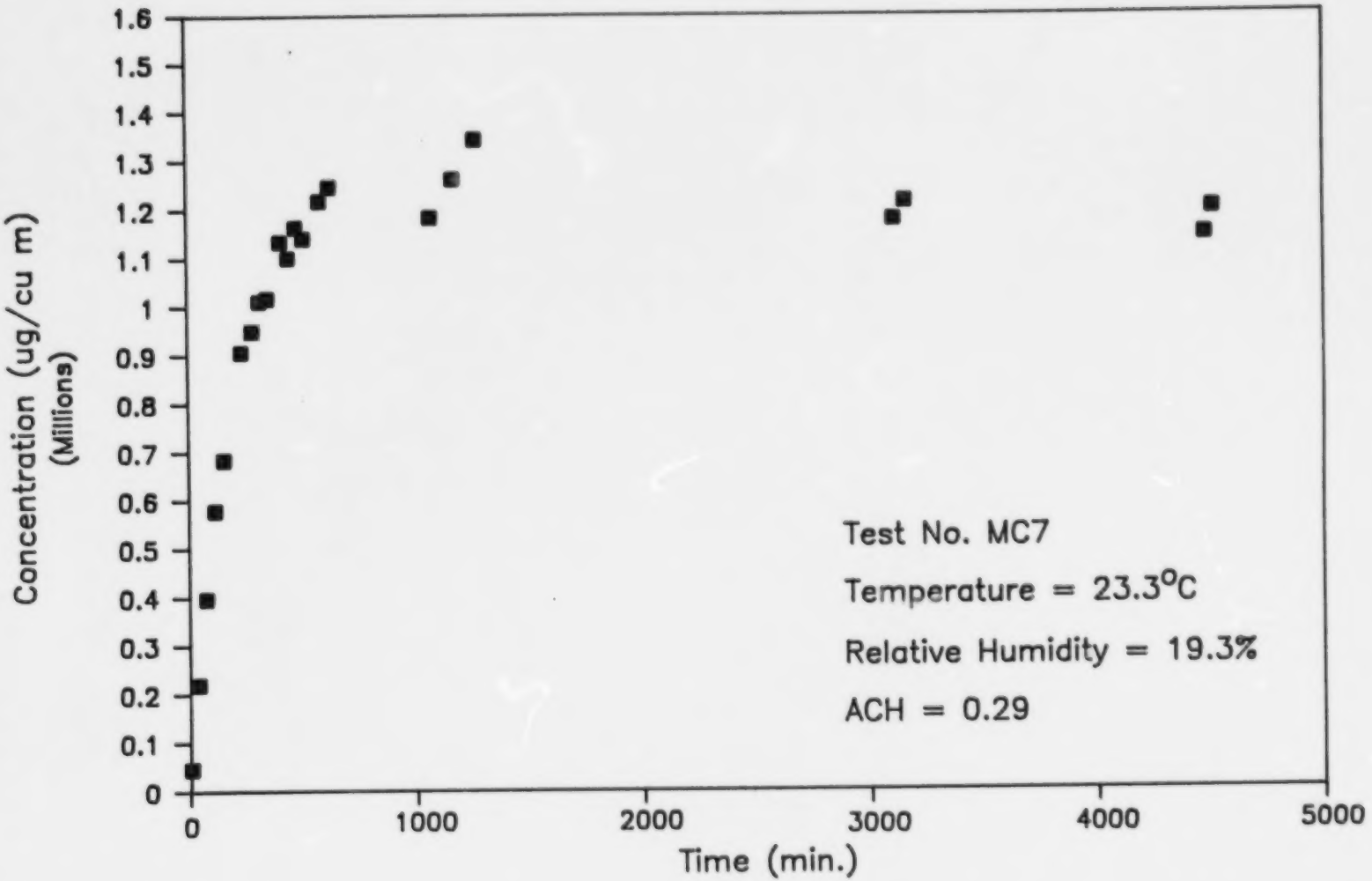

Figure 1. Chamber Concentration vs Time

Moth Crystal Cake (p–Dichlorobenzene)

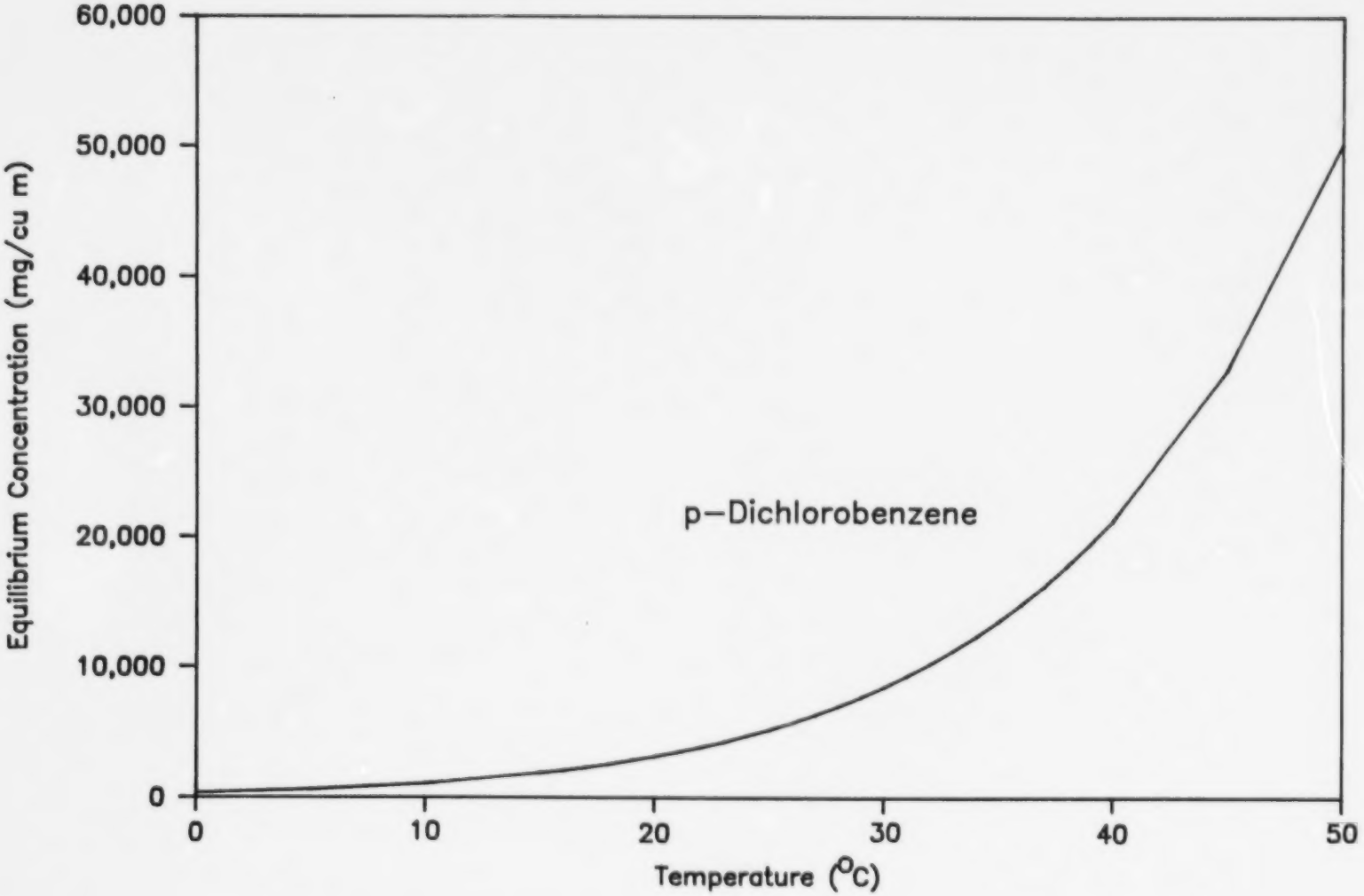

Figure 2. Equilibrium Concentration vs Temperature

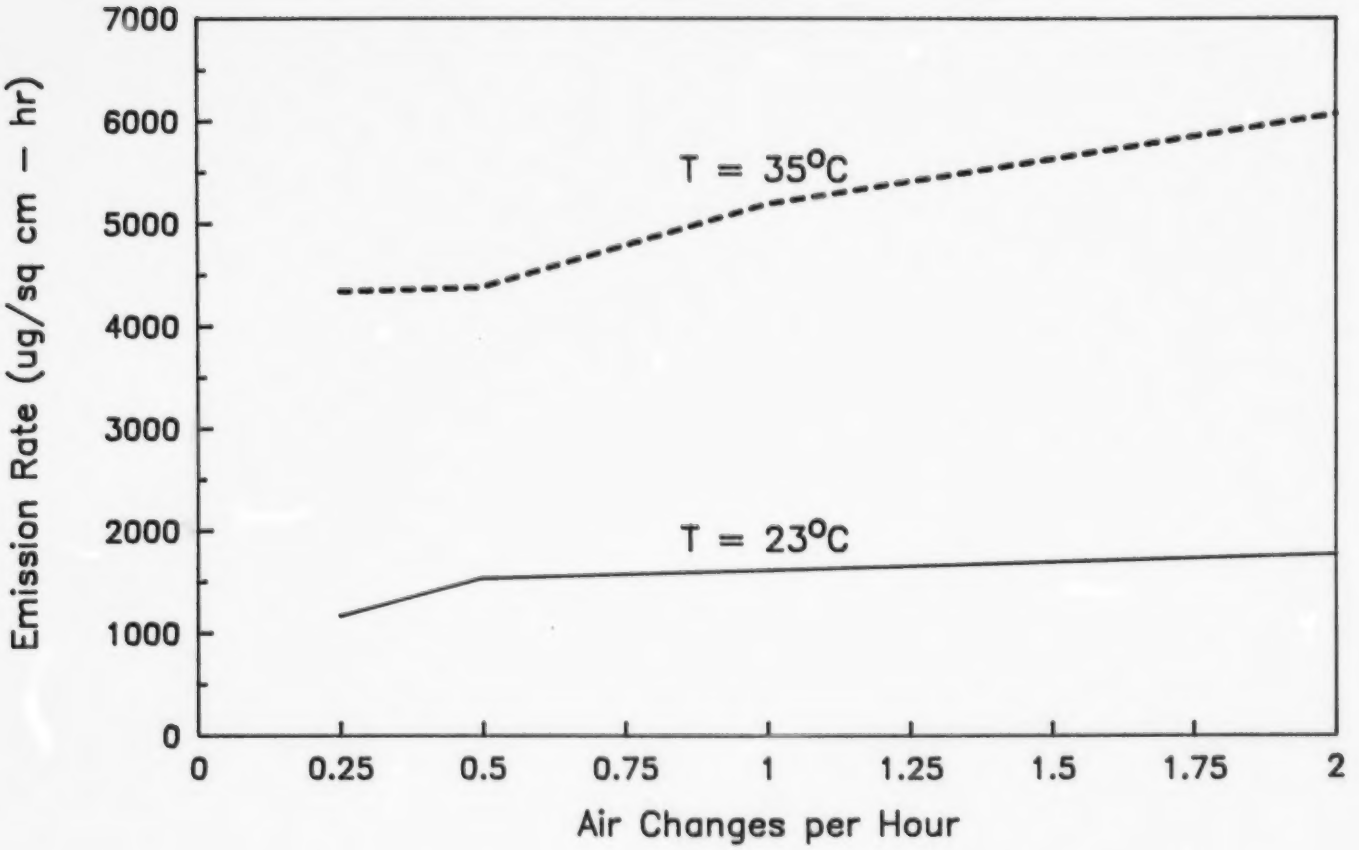

Figure 3. Emission Rate vs Air Exchange Rate

Moth Crystal Cake (p-Dichlorobenzene)

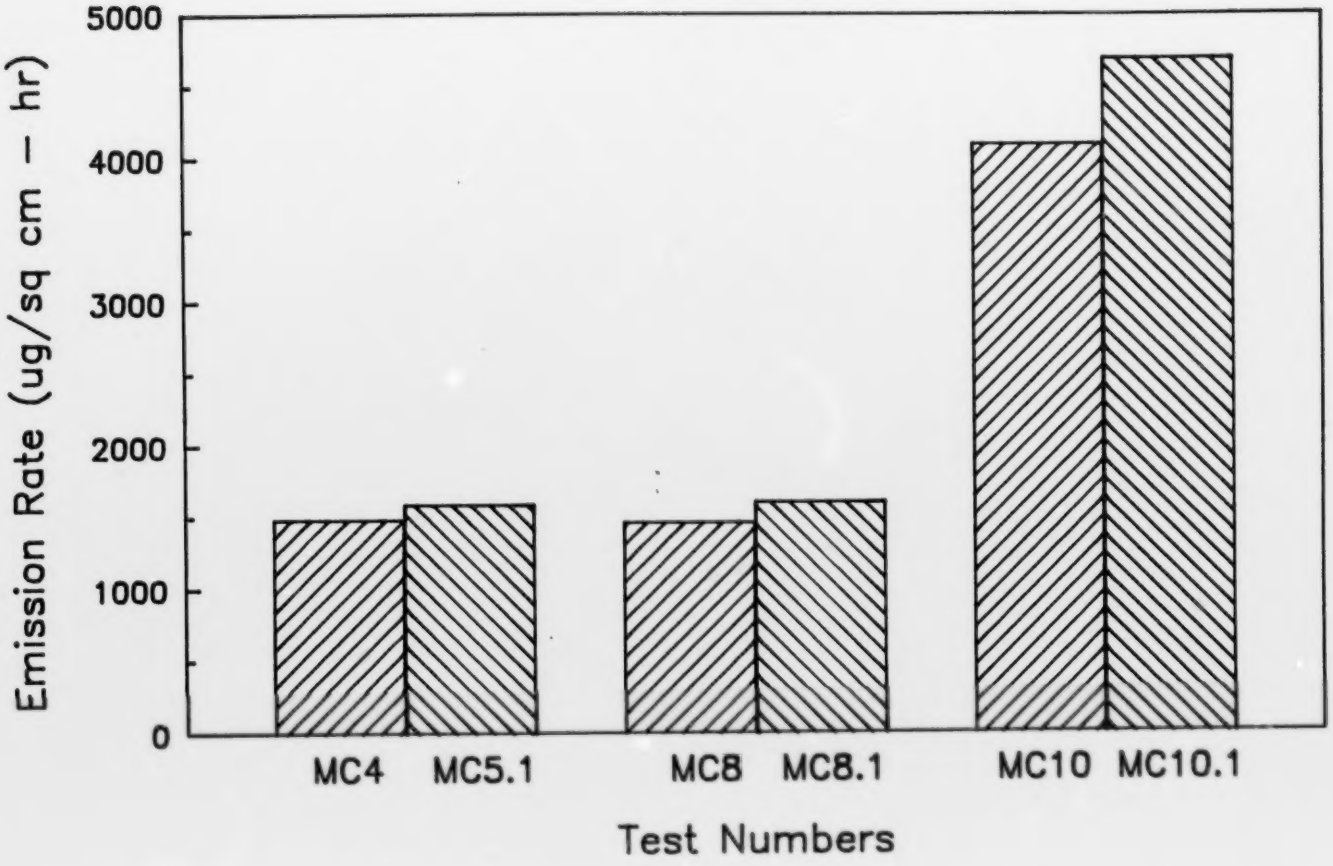

Figure 4. Emission Rates – Replicate Tests
Moth Crystal Cakes (p–Dichlorobenzene)